The Relationship Existing between the Weight of a Falling Drop and the Diameter of the Tip from which it Falls

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

BY

JESSIE YEREANCE CANN, A.B., A.M.

NEW YORK CITY

1911

EASTON, PA.:
ESCHENBACH PRINTING COMPANY.
1911.

The Relationship Existing between the Weight of a Falling Drop and the Diameter of the Tip from which it Falls

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

BY

JESSIE YEREANCE CANN, A.B., A.M.

NEW YORK CITY

1911

EASTON, PA.:
ESCHENBACH PRINTING COMPANY.
1911.

ACKNOWLEDGMENT.

The following investigation was suggested by and carried out under the direction of Professor J. Livingston R. Morgan. The author desires to extend her sincere thanks and appreciation to Professor Morgan for his helpful assistance, advice and encouragement during the course of the work.

J. Y. C.

The Relationship Existing between the Weight of a Falling Drop and the Diameter of the Tip from which it Falls

INTRODUCTION.

Object of the Investigation.

In 1864, Thomas Tate,[1] as the result of his experiments with water, announced the following laws:

I. Other things being the same, the weight of a drop of liquid (falling from a tube) is proportional to the diameter of the tube in which it is formed.

II. The weight of the drop is in proportion to the weight which would be raised in a tube with a bore equal to the outer diameter by capillary action.

III. The weight of a drop of liquid, other things being the same, is diminished by an augmentation of temperature.

Tate's experiments were all made with thin-walled glass tubing, varying in diameter from 0.1–0.7 of an inch, the orifice in each case being ground to a "sharp edge, so that the tube at the part in contact with the liquid might be regarded as indefinitely thin." His weights were calculated from the weight of from five to ten drops of liquid, which formed at intervals of forty seconds, and were collected in a weighed beaker.

Tate's law is generally accepted as equivalent to the expression

$$w = 2 \pi r \gamma,$$

where w is the weight of the falling drop, r the radius of the tube on which it forms, and γ is the surface tension of the liquid. This expression is not exactly as Tate intended it to be formulated, for his law simply states a proportionality; so that the expression should be

$$w = 2 \pi r \gamma K,$$

where K is some constant which will transform the proportionality into an equality.

[1] *Phil. Mag.*, 4th Ser., 27, 176 (1864).

It has also been shown by Morgan and Stevenson,[1] Morgan and Higgins[2] and Morgan and Thomssen[3] contrary to the conclusions of all other workers since Tate that the weight of a single drop of a non-associated liquid falling from a definite tip is regulated by the following laws:

I. The quantity $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ (w = weight of drop in milligrams, M = molecular weight, d = density) is a linear function of the temperature, becoming zero at a point 6° below the observed critical temperature or a fictitious critical temperature. Expressed mathematically we have then (in the form of Ramsay and Shields, for surface tension)

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k(t_c - t - 6)$$

where t_c is the critical temperature (observed or fictitious) and t is the temperature of observation and k a universal constant, defined by the equation

$$k = \frac{w_1\left(\frac{M}{d}\right)^{\frac{2}{3}} - w_2\left(\frac{M}{d}\right)^{\frac{2}{3}}}{t_2 - t_1}$$

although, as has been shown by Morgan,[3] it should not be calculated in this way, owing to the multiplication of error, but from $w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B(288.5 - t - 6)$ for benzene once for all.

II. The temperature coefficient of the function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$ *i. e.*, the k_B of the above equation is a universal constant for such liquids, leading, as has been shown by Morgan,[3] to the same value of t_c for any one non-associated liquid at all temperatures of observation.

It has further been shown by Morgan that the above laws hold also when applied to the results of Ramsay and Shields of surface tension, thus confirming Tate's second law.

[1] *J. A. C. S.*, 30, 360–376 (1908).
[2] *Ibid.*, 30, 1055–68 (1908).
[3] *Ibid.*, May, 1911.

The object of this investigation was to establish conclusively the truth of the first of the above laws, *i. e.*, to make an exhaustive study of the relationship existing between the weight of a falling drop and the diameter of the tip from which it falls. For this purpose sixteen different tips were employed, varying in size from about 3 mm. to approximately 8 mm. in diameter. Five representative liquids, including that with practically the largest, as well as that with the smallest possible drop volume, were chosen and the relationship between the drop weights, and the different sized tips studied exhaustively.

Apparatus and Method.

The apparatus used in this work is a new and simple form designed by Morgan[1] and especially adapted to the general needs of the investigator in other lines of chemistry. By it the weight of a falling drop of any liquid from any desired tip can be found at various temperatures, up to within a few degrees of the boiling point, with very great accuracy, every possible form of variable error having been foreseen and avoided. As the results of this work show, the method is indeed one of very great accuracy.

In order to exclude any variation in the results due to changing temperature, all measurements were made in a constant temperature bath. This was of the Ostwald gas type with a transparent bath, stirred by a small electric motor. The temperature employed was 27.8° C., the greatest variation recorded being $\pm 0.03°$. The thermometer used here was a certified one reading in fiftieths of a degree.

The five representative non-associated liquids were *quinoline, pyridine, benzene, ether and carbon tetrachloride.* These five liquids were considered the best because of their great differences in density, surface tension and general physical properties (*i. e.*, viscosity, etc.).

The weight of the drop was obtained by finding, first, that of thirty or more drops, in the following manner. The liquid is sucked over from the supply vessel into the capillary

[1] *J. A. C. S.*, March, 1911.

tubing, and allowed to form a drop on the tip. This drop is held at as nearly as possible its maximum size for 5 minutes, so that the vessel may become saturated with the vapor of the liquid used. Next, thirty consecutive drops are allowed to fall each drop falling of its *own weight alone*, and the time of the entire determination noted. Then the vessel with the vapor and thirty drops is weighed, being wiped with cheese-cloth to constant weight. After the apparatus has been set up again, and has assumed the temperature of the bath by remaining in it for a half hour or more, another determination, a "blank" is taken. This time the liquid is sucked over in the same manner as before, the drop being allowed to hang five minutes, but only five consecutive drops are allowed to fall, the sixth drop being held on the tip without falling for the balance of the time consumed by the first determination. In this way the liquid in the weighing vessel in each determination is exposed for the same length of time to the same evaporating influence both for the hanging drop and the liquid which has fallen, so that the total loss is the same in both cases. By subtracting this 5-drop blank from the 30-drop determination, the weight of one drop is obtained, after dividing the difference by 25. Exactly the same method is to be employed with each liquid used.

The densities used were those determined by Morgan and Higgins.

Liquids.

The *benzene* used in this work was Kahlbaum's special *K*. The *quinoline* was distilled frequently, for when it contains water the results are too low, while when allowed to stand it decomposes, becoming thicker and yellow, and giving high results. Because of the "sticky" nature of quinoline great care had to be taken each time between determinations to clean the capillary tube very thoroughly, and then to prevent liquid rising until the first drop was run over, so that no threads of liquid would be spurted over before the drop, and thus cause the weight to be too large. The *pyridine* used was Kahlbaum's special *K*, and remained unchanged—pure and colorless—throughout the entire period of work.

It was found in working with pyridine, particularly with the larger tips, that each drop had to be drawn back into the capillary tube, before being allowed to fall, so that each drop would be exactly like the first drop. It was apparent to the eye in these cases that the regular procedure caused the successive drops to grow smaller, and that the liquid did not extend out to the edge of the tip, and hence would give too low a result. The *carbon tetrachloride* used was from Baker and was redistilled often. Great care had to be taken in making determinations with this liquid, for the drop volume and surface tension are so small that unless the drop is perfectly controlled at the moment of fall the result will be too large. With tips larger than 4.5 mm. this control is extremely difficult, if possible at all on this form of apparatus, and the results obtained are always too high. This perfect control, however, is one of the essential principles of the drop weight method. The *ether* was from Kahlbaum, and was always redistilled several times before a determination. Without redistillation the results are always found to be too high.

Results.

In Tables I–V are the experimental results obtained with the sixteen tips used for the liquids studied, together with the values of the function $w\left(\frac{M}{d}\right)^{\frac{2}{3}}$, where w is the drop weight and d the density, both at the same temperature, while M is the molecular weight.

TABLE I.—BENZENE.

Diameter of tip. Mm.	Wt. 30 drops and vessel. Grams.	Av. wt. of 30 drops and vessel. Grams.	Wt. 5 drops and vessel. Grams.	Av. wt. of 5 drops and vessel. Grams.	Av. wt. of 1 drop. Mgs.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.
	10.3560		9.9222			
3.048	10.3561	10.35606	9.9222	9.9222	17.355	347.51
	10.3561					
	11.1960		10.6569			
3.929	11.1960	11.1960	10.6569	10.6569	21.564	431.77
	11.1960					

TABLE I.—(*Continued*).

	10.4067		9.8585			
	10.4067					
4.000	10.4071	10.40695	9.8587	9.8586	21.934	439.18
	10.4073					
	10.0359		9.4292			
4.514	10.0359	10.03586	9.4291	9.42915	24.269	485.72
	10.0358					
	9.9938		9.3626			
	9.9938		9.3626			
4.695	9.9936	9.99373	9.3626	9.3626	25.245	505.47
	9.9937					
	10.8887		10.2198			
4.978	10.8887	10.88863	10.2198	10.2198	26.753	535.67
	10.8885					
	(25 drops)					
	11.2625		10.6918			
	11.2622					
5.306	11.2619	11.26233	10.6918	10.6918	28.526	571.17
	11.2627					
	11.2137		10.4754			
			10.4756			
5.501	11.2137	11.2137	10.4755	10.4755	29.528	591.23
	11.2137		10.4755			
	9.7253		8.9873			
5.500	9.7255	9.7256	8.9873	8.9873	29.532	591.31
	9.7260					
	9.7554		8.9922			
5.689	9.7555	9.7554	8.9920	8.9921	30.532	611.33
	9.7553					
	11.3907		10.6067			
5.845	11.3905	11.39056	10.6068	10.60683	31.349	627.70
	11.3905		10.6070			
	11.3815		10.7159			
6.200	11.3816	11.38163	10.7159	10.7159	33.287	666.48
	11.3818					

Table I.—(*Continued*).

	(25 drops)					
	11.5351		10.8287			
	11.5357					
	11.5357		10.8282			
	11.5357					
6.550	11.5352	11.53548	10.8285	10.82846	35.351	707.82
	11.5357					
	11.5357					
	11.5351					
	(25 drops)					
	10.4305		9.6872			
	10.4302					
6.844	10.4299	10.43023	9.6870	9.6871	37.156	743.97
	10.4303					
	(25 drops)					
	11.4210		10.6057			
7.387	11.4207	11.42073	10.6058	10.60575	10.749	815.91
	11.4205					
	(25 drops)					
	11.4978		10.6215			
7.859	11.4980	11.4981	10.6215	10.6215	43.83	877.58
	11.4985					

Table II.—Quinoline.

Diameter of tip. Mm.	Wt. 30 drops and vessel. Grams.	Av. wt. of 30 drops and vessel. Grams.	Wt. 5 drops and vessel. Grams.	Av. wt. of 5 drops and vessel. Grams.	Av. wt. of 1 drop Mg.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.
	10.6755		9.9739			
3.048	10.6759	10.67566	9.9743	9.9741	28.063	677.48
	10.6756		9.9741			
	10.8235		9.9594			
3.929	10.8238	10.82376	9.9595	9.95945	34.573	834.62
	10.8240					
	10.8021		9.9229			
4.000	10.8020	10.8021	9.9230	9.92296	35.165	848.93
	10.8022		9.9230			
	(20 drops)					
	10.0749		9.4979			
	10.0749					
4.514	10.0755	10.0752	9.4979	9.4979	38.487	929.11
	10.0755					

TABLE II.—(*Continued*).

	(20 drops)					
	11.4198		10.7825			
4.978	11.4196	11.4197	10.7825	10.7825	42.48	1025.52
	11.4197					
	11.7336		10.5604			
5.501	11.7330	11.7333	10.5604	10.5604	46.916	1132.61
	11.7333					
	10.2444		9.0713			
5.500	10.2443	10.2444	9.0715	9.0714	46.92	1132.71
	10.2445		9.0714			
	10.2932		9.0802			
5.689	10.2939					
	10.2938	10.2935	9.0798	9.0800	48.54	1171.00
	10.2931					
	11.6891		10.6955			
5.845	11.6892	11.68923	10.6953	10.6954	49.692	1199.61
	11.6894					
	(20 drops)					
	11.6005		10.8104			
6.200	11.6010	11.6007	10.8106	10.8105	52.68	1271.73
	11.6006					
	(20 drops)					
	11.7617		10.9261			
6.550	11.7611					
	11.7617	11.76158	10.9261	10.9261	55.698	1344.62
	11.7618					
	(25 drops)					
	10.6615		9.7894			
6.844	10.6605	10.66106	9.7894	9.7894	58.111	1402.87
	10.6612					
	(20 drops)					
	11.6620		10.7150			
7.387	11.6615	11.66186	10.7150	10.7150	63.124	1523.90
	11.6621					
	(20 drops)					
	11.7521		10.7372			
7.859	11.7517	11.75176	10.7372	10.7372	67.638	1632.10
	11.7515					

TABLE III.—PYRIDINE.

Diameter of tip. Mm.	Wt. 30 drops and vessel. Grams.	Av. wt. of 30 drops and vessel. Grams.	Wt. 5 drops and vessel. Grams.	Av. Wt. of 5 drops and vessel. Grams.	Av. wt. of 1 drop Mg.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.
	10.5144		9.9470			
3.048	10.5143	10.51446	9.9470	9.9470	22.699	425.42
	10.5147					
	10.6369		9.9288			
3.929	10.6368	10.6369	9.9287	9.9288	28.324	530.85
	10.6370		9.9289			
	10.7625		10.0422			
4.000	10.7628	10.76246	10.0422	10.0422	28.81	539.96
	10.7621					
	10.2604		9.4654			
4.514	10.2610	10.2606	9.4651	9.46533	31.811	596.20
	10.2604		9.4655			
	11.1390		10.2609			
4.978	11.1392	11.13913	10.2605	10.2607	35.137	658.54
	11.1392					
	11.1435		10.1744			
5.501	11.1436	11.1435	10.1745	10.17445	38.762	726.48
	11.1434					
	10.0003		9.0311			
5.500	10.0004	10.00033	9.0312	9.03116	38.767	726.57
	10.0003		9.0312			
	10.0387		9.0363			
5.689	10.0385	10.0384	9.0368	9.03655	40.074	751.07
	10.0380					
	11.6846		10.6545			
5.845	11.6840	11.68446	10.6546	10.65455	41.197	772.11
	11.6848					
	(25 drops)					
	11.8020		10.8792			
6.550	11.8029					
	11.8022	11.80227	10.8795	10.87935	46.146	864.88
	11.8020					

TABLE III.—(*Continued*).

	(25 drops)					
6.844	10.7045 10.7044 10.7046	10.7045	9.7405 9.7405	9.7405	48.20	903.37
	(25 drops)					
7.387	11.7069 11.7069 11.7069	11.7069	10.6599 10.6599	10.6599	52.35	981.15
	(25 drops)					
7.859	11.8022 11.8023 11.8022	11.80223	10.6807 10.6806 10.6807	10.68066	56.078	1051.02

TABLE IV.—CARBON TETRACHLORIDE.

Diameter of tip. Mm.	Wt. 30 drops and vessel. Grams.	Av. wt. of 30 drops and vessel. Grams.	Wt. 5 drops and vessel. Grams.	Av. wt. of 5 drops and vessel. Grams.	Av. wt. of 1 drop. Mg.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$
	(50 drops)		(10 drops)			
3.048	10.5284 10.5280 10.5289 10.5279	10.5283	9.9077 9.9077	9.9077	15.515	328.97
3.929	10.3811 10.3812 10.3810	10.3811	9.8895 9.8896 9.8894	9.8895	19.664	416.94
	(50 drops)		(10 drops)			
4.000	8.5932 8.5937 8.5930 8.5931	8.59323	7.7934 7.7932	7.7933	19.998	424.03
	(50 drops)					
4.514	8.1205 8.1208 8.1203 8.1204	8.1205	7.1108 7.1108	7.1108	22.438	475.76
4.695	7.9593 7.9593 7.9594 7.9593	7.95933	7.3713 7.3710 7.3710 7.3708 7.3718	7.37118	23.526	498.83

TABLE IV.—(*Continued*)

4.978	9.5975 9.5977 9.5980 9.5978	9.59775	8.9709 8.9710 8.9714	8.9711	25.066	531.46
5.306	11.3661 11.3661	11.3661	10.6910 10.6910	10.6910	27.004	572.58
5.501	10.8320 10.8322 10.8321	10.8321	10.1265 10.1265	10.1265	28.224	598.45
5.500	9.6945 9.6944	9.69445	8.9873 8.9871	8.9872	28.29	599.82
5.689	9.7327	9.7327	8.9938	8.9938	29.556	626.69
5.845	11.3760 11.3762 11.3761	11.3761	10.6089 10.6084	10.60865	30.698	650.90
6.200	11.5330	11.5330	10.7172	10.7172	32.632	691.91
6.550	11.6985	11.6985	10.8317	10.8317	34.672	735.17
6.844	10.6061	10.6061	9.6906	9.6906	36.62	776.47

TABLE V.—ETHER.

Diameter of tip. Mm.	Wt. 30 drops and vessel. Grams.	Av. wt. of 30 drops and vessel. Grams.	Wt. 5 drops and vessel. Grams.	Av. wt. of 5 drops. and vessel. Grams.	Av. wt. of 1 drop. Mg.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.
	(50 drops)		(10 drops)			
3.048	7.6045 7.6045	7.6045	7.2107 7.2109	7.2108	9.843	219.23
3.929	8.7205 8.7206 8.7204	8.7205	8.4134 8.4133 8.4135	8.4134	12.284	273.61
	(50 drops)		(11 drops)			
4.000	8.2272 8.2272 8.2279 8.2274	8.22743	7.7400 7.7401 7.7400	7.74003	12.497	278.36

TABLE V.—(*Continued*).

	(50 drops)		(10 drops)			
4.514	9.1339 9.1344 9.1347 9.1349	9.13448	8.5816 8.5818 8.5820 8.5823 8.5820	8.58194	13.813	307.67
4.695	7.7829 7.7831 7.7830	7.7830	7.4019 7.4019 7.4020	7.40193	15.243	339.51
5.501	7.6328 7.6327 7.6329	7.6328	7.2122 7.2121 7.2122	7.21216	16.825	374.76
5.500	7.7575 7.7574 7.7575	7.75746	7.3367 7.3369 7.3368	7.3368	16.827	374.79
5.689	7.7775 7.7776 7.7775	7.77753	7.3400 7.3400	7.3400	17.501	389.82
5.845	7.7895 7.7894 7.7896	7.7895	7.3394 7.3393 7.3395	7.3394	18.004	401.02
6.550	8.9719 8.9720 8.9720	8.97196	8.4555 8.4556 8.4554	8.4555	20.659	460.14
6.844	8.6478 8.6480 8.6479	8.6479	8.1043 8.1045 8.1044	8.1044	21.74	484.23
7.387	8.6256 8.6257 8.6255	8.6256	8.0254 8.0255 8.0253	8.0254	24.008	534.75
7.859	8.4755 8.4759 8.4750	8.47546	7.8232 7.8230	7.8231	26.095	581.23

On all three tips below 4.514 mm. benzene, quinoline, pyridine and ether showed drop profiles which were very much larger at the bottom of the drop than at the top or than the diameter of the tip itself, so that on all these tips we should expect the results to be non-concordant when various liquids are compared, for the amount of the bulging, and consequently of the weight of the liquid falling is here independent of the diameter of the tip from which it falls. *On the tips from 4.514 up to and including 5.501 the control of the drop was perfect with all the liquids except carbon tetrachloride, and at most the profile of the drop showed that the edges of the lower part are simply a continuation of the edges of the tip and none extends beyond.*

Carbon tetrachloride can only be perfectly controlled on tip of 4.514 and on the two sizes below, the drop on all the larger tips spurting at the last moment and carrying down with it an excess of liquid. This is due to the small drop volume, together with the small surface tension of this liquid, which makes the drop at its lower extremity very small, and very liable to break down.

It is to be remembered here that the perfect control is lost only on the form of apparatus in question, for the long capillary burette used by Morgan and Higgins would undoubtedly show perfect control on considerably larger tips, for the long tail of liquid in the narrow capillary only allows a very slow formation of the drop at best.

Ether is found to be difficultly controlled on the 5.689; while only on the larger ones is trouble experienced with benzene, pyridine and quinoline. We should expect then on the tips from 3.929 up to and including 4.514 that carbon tetrachloride would be the criterion for other like liquids, for its drop volume is so small that the edges of the drop never extend beyond lines parallel to the edges of the tip itself.

As soon as perfect control is lost, the drop which falls is too large for it does not fall of its *own weight alone*, but has projected with it some of the liquid which under perfect control would remain on the tip. This increase in weight continues to increase with the diameter of the tip until the

maximum drop volume has been attained, after which the edges of the drop pull away from the tip; when, provided the control were still perfect, too small a drop for that tip would result. As the control, however, is not perfect, we should expect the value to become too high as control is lost, then to become correct when lack of control is just balanced by the decreasing effect of the drop pulling away from the tip; and finally the drop would probably remain of the same weight on all larger tips. Although the diameters of the above tips were measured on a dividing engine, the mean of a number of determinations on each of three diameters being taken, the accuracy is certainly not much greater than 0.01 mm. owing to the fact that the tips were never perfectly circular in section, and in some cases flaws had developed in the edge which made the measurement difficult, although probably it affected the drop weight but slightly.[1] In

TABLE VI.

Diameter of tip. Mm.	Values for $\frac{w}{d}$. Benzene. Mg.	Quinoline. Mg.	Pyridine. Mg.	CCl_4. Mg.	Ether. Mg.
3.048	5.6970	9.2069	7.4470	5.0902	3.2291
3.929	5.4884	8.7992	7.2089	5.0008	3.1265
4.000	5.4835	8.7913	7.2025	4.9995	3.1243
4.514	5.3762	8.5260	7.0471	4.9706	3.0601
4.695	5.3769			5.0108	
4.978	5.3743	8.5335	7.0585	[5.0353]	3.0620
5.306	5.3752			5.0883	
5.501	5.3677	8.5286	7.0463	5.1307	3.0585
5.500	5.3694	8.5309	7.0484	5.1436	3.0593
5.689	5.3668	8.5126	7.0441	5.1952	[3.0763]
5.845	5.3630	8.5009	7.0477	5.2516	3.0880
6.200	5.3688	8.4967		5.2621	
6.550	[5.3971]	8.5035	7.0452	5.2934	3.1532
6.844	5.4290	8.4908	7.0426	5.3506	3.1779
7.387	5.5157	[8.5447]	[7.0863]		3.2498
7.859	5.5766	8.6058	7.1340		3.3201

Table VI are given the values of w/d for each liquid on each tip. From this all those things mentioned above as to the

[1] In this connection it may be said that the 5.501 tip is the one used by Morgan and Thomssen, the results here being slightly lower, due to slight flaws, presumably, which have since developed.

bulging or the loss of control are made clearer than they would be in a small curve, for the difference there would hardly be noticeable.

It will be noted here that from 3.929 to 4.514 the value of *w/d* for *carbon tetrachloride* is constant and then increases continually with the size of the tip, showing the effect of lack of control, and later the combination of that with the pulling away of the drop from the edge; while for all the other liquids, on the contrary, up to 4.514 the value decreases then remains constant for a greater or less variation in diameter. The loss of control of *ether* is first observed on the 5.689 tip, while *benzene* is lost on the 6.55, and *pyridine* and *quinoline* on the 7.387.

TABLE VII.—NORMAL BENZENE CONSTANTS.

Diameter of tip. Mm.	$w\left(\frac{M}{d}\right)^{\frac{2}{3}}$.	$k = \dfrac{w\left(\frac{M}{d}\right)^{\frac{2}{3}}}{288.5 - 27.8 - 6}$.
3.048	347.51	1.3644
3.929	431.77	1.6952
4.000	439.18	1.7243
4.514	485.72	1.9078
4.695	505.47	1.9846
4.978	535.67	2.1032
5.306	571.17	2.2425
5.501	591.23	2.3213
5.500	591.31	2.3216
5.689	611.33	2.4002
5.845	627.70	2.4645
6.200	666.48	2.6168
6.550	707.82	2.7791
6.844	743.97	2.9210
7.387	815.91	3.2034
7.859	877.58	3.4456

The 4.514 tip is the only one which gives correct results for carbon tetrachloride, for above this tip the results are too high, due to lack of control; while below it, it is impossible to use benzene as the standard because of the bulging of the drop. The carbon tetrachloride *k* is then the only true one for small tips, and hence in the future will be the liquid used for the standardization of small tips when they are used for

determining the drop weights of liquids similar to that of carbon tetrachloride, *i. e.*, liquids with a very high density and small surface tension. The value of t_c is then to be taken as 283.15° as found on the 4.514 tip, and the normal value of the constant k of the tip calculated from it.

In Table VII are the k_B values found from benzene by use of the formula

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k_B(288.5 - 27.8 - 6)$$

Wherever both benzene and the other liquid give constant results of $\frac{\text{weight}}{\text{diameter}}$ we would expect to find a constant value of k necessary to give the values of t_c as found from the work of Morgan and Higgins by Morgan,[1] on substituting the values of M and d for that liquid in

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = k(t_c - t - 6).$$

These t_c values are 346.6° for pyridine, 521.3° for quinoline, 195° for ether and 283.2° for carbon tetrachloride.

Table VIII.—$k = \dfrac{w\left(\frac{M}{d}\right)^{\frac{2}{3}}}{t_c - 27.8 - 6}$

Diameter of tip. mm.	Benzene.	Quinoline.	Pyridine.	Ether.	CCl_4.
4.514	1.9078	1.90~~7~~60	1.90~~7~~61	1.9091	1.9081
4.695	1.9846				[2.0004]
4.978	2.1032	2.10~~7~~36	2.10~~7~~54	2.1066	[2.1311]
5.307	2.2425				[2.2777]
5.500	2.3216	2.32~~7~~35	2.3~~1~~230	2.3256	[2.3856]
5.501	2.3213	2.3233	2.3230	2.3254	[2.3801]
5.689	2.4002	2.4037	2.4012	[2.4188]	

In Table VIII are given those k values for the tips from 4.514–5.501 inclusive, between which we should expect the liquids to be concordant in result, with the exception of carbon tetrachloride, since the values of $\frac{\text{weight}}{\text{diameter}}$ are constant

[1] *J. A. C. S.*, May, 1911.

on them. The value of this latter on the 4.695 tip shows the effect of the lack of perfect control which was noted when the determination was made.

Since, as has been shown by Morgan, surface tension in dynes can be found from drop weight in milligrams by aid of the proportion

$$\gamma : w :: K_B : k_B,$$

where K_B is the value found from Ramsay and Shields very accurate benzene values, calling $t_c = 288.5°$, *i. e.*, 2.1012; while k_B is the similarly determined value for drop weight on the tip in question (see Table VIII).

Table IX contains the values of surface tension in dynes, calculated from drop weight in milligrams by aid of the above relation for the tips considered in Table VIII.

TABLE IX.—SURFACE TENSIONS.

Diameter of tip.	k_B.	Quinoline.	Pyridine.	Ether.	CCl_4.
4.514	1.9078	42.39	35.04	15.22	24.71
4.695	1.9846				
4.978	2.1032	42.44	35.10	15.23	
5.307	2.2425				
5.501	2.3213	42.47	35.09	15.23	
5.500	2.3216	42.47	35.09	15.23	
5.689	2.4002	42.49	35.08	[15.32]	
	Average,	42.45	35.08	15.23	

TABLE X.—*k* VALUES.

Diameter of tip. Mm.	Benzene.	Quinoline.	Pyridine.	Ether.	CCl_4.
3.048	1.3644	1.3897	1.3601	1.3603	1.3194
3.929	1.6952	1.7121	1.6971	1.6977	1.6722
4.000	1.7243	1.7414	1.7264	1.7272	1.7007
5.689	2.4002	2.4037	2.4012	2.4188	2.4930
5.845	2.4645	2.4608	2.4685	2.4883	2.5893
6.200	2.6168	2.6088			2.7524
6.550	2.7791	2.7582	2.7651	2.8552	2.9245
6.844	2.9210	2.8777	2.8881	3.0046	3.0888
7.387	3.3034	3.1260	3.1368	3.3181	
7.859	3.4456	3.3495	3.3601	3.6065	

Table X contains the k values and Table XI the γ values calculated similarly for the other tips, which from their $\frac{\text{weight}}{\text{diameter}}$ relations should not be perfectly satisfactory.

It will be noted here that the results are exactly what has already been shown by the simpler w/d ratios, so that we need not discuss them further.

TABLE XI.—SURFACE TENSIONS.

Diameter. of tip. Mm.	Benzene.	Quinoline.	Pyridine.	Ether.	CCl_4.
3.048	26.73	43.21	34.96	15.16	23.89
3.929	26.73	42.85	35.10	15.22	24.37
4.000	26.73	42.85	35.11	15.23	24.37
5.689	26.73	42.49	35.08	15.32	25.87
5.845	26.73	42.37	35.12	15.35	26.17
6.200	26.73	42.30			26.20
6.550	26.73	42.11	34.89	15.62	26.21
6.844	26.73	41.80	34.67	15.64	26.34
7.387	26.73	41.40	34.34	15.75	
7.859	26.73	41.25	34.20	15.91	

For benzene, using the value of w/d (see Table VI) we find the following relationships (holding for tips from 4.514 to 5.501 inclusive),

$$w = 5.372 \times 2r$$

and

$$w = 1.710 \times \pi \times 2r$$

where w is given in milligrams and r in millimeters. The relationship existing between diameter, drop weight and surface tension in dynes per cm. (found from the above, knowing further that w = constant $\times$ γ) *for any liquid* is then

$$w = 0.063972 \times (2r)\,\pi\,\gamma.$$

Although this relationship was found for benzene it must hold for all the other liquids since the assumption in obtaining it was only that w is proportional to γ.

In Table XII are given the values of γ as calculated from the above equation.

TABLE XII.—SURFACE TENSIONS.

Diameter of tip. Mm.	Benzene.	Quinoline.	Pyridine.	CCl_4.	Ether.
4.514	26.75	42.42	35.06	24.73	15.23
4.695	26.75				
4.978	26.74	42.46	35.12		15.24
5.306	26.75				
5.500	26.72	42.45	35.07		15.22
5.501	26.71	42.44	35.06		15.22
5.689	26.70	42.45	35.05		[15.31]
Av.,	26.73	42.44	35.07	24.73	15.23

Conclusions.

I. The drop weights of benzene, quinoline, pyridine, ether and carbon tetrachloride have been determined at a constant temperature from sixteen different tips varying in size from 3.048 to 7.859 mm. in diameter.

II. All liquids from water, forming practically the largest drop volume to carbon tetrachloride, practically the smallest, follow Tate's law as to proportionality with surface tension on a tip of 4.514 mm. diameter; while, excluding carbon tetrachloride and a few similar liquids with small surface tensions and large densities, the law is found to hold rigidly on tips between 4.514 and 5.501 mm.

III. Smaller tips than 4.514 are adapted only to related liquids when the lower end of the drop bulges in the same way, or those which like carbon tetrachloride form on them normal looking drops similar to those of other liquids on the larger tips.

IV. Tips larger than 5.501 will also hold for similar liquids only, for here it is simply a question of the perfection in the control of the drop.

V. All these things can be observed by closely watching the drop; and a liquid can be said to be satisfactory or not as soon as its drop profile on the tip in question is observed. This is also shown for a series of tips by the values of the ratios $\frac{\text{weight}}{\text{diameter}}$.

VI. Surface tensions in dynes per cm. calculated from drop weight in milligrams by multiplication with the ratio of k_γ / k_w show the same values for the liquids considered when calculated for all tips, the variation being considerably smaller than that from capillary rise by the same observers with different tubes.

VII. It is found that drop weight in milligrams, diameter of the tip in millimeters and surface tension in dynes are related, for tips from 4.514 to 5.501 by the following equation

$$w = 0.063972\ (2\ r)\ \pi\ \gamma$$

VIII. It is shown clearly why such a law cannot hold for all liquids on smaller or larger tips than these, but it must be recognized that even on tips beyond these, in either direction, that the results, in terms of surface tension, agree with the others fully as well as do those values determined by aid of capillary rise by various observers.

BIOGRAPHY.

Jessie Yereance Cann was born May 17, 1883, in Newark, New Jersey. In June 1901 she graduated from the Newark High School, and was awarded a four-year scholarship in the Woman's College of Baltimore (Goucher College). She completed her college course in three years, receiving the degree of A.B. in June, 1904. During the years 1904–1909 she taught Science in the Belleville (N. J.) High School. She was a graduate student in Physical Chemistry at Columbia University during the years 1909–1911, as well as during the Summer Sessions of 1907, 1908, 1909 and 1910; and the holder of a Curtis Scholarship 1909–1910, receiving the degree of A.M. in June, 1910.